LESSON 1 **THERMODYNAMICS OF SURFACES**

1. Review of thermodynamics

a) Principles

- First principle (only reversible processes will be considered.): $\bar{\delta}Q = \delta U + \bar{\delta}W$

  ($\bar{\delta}$ symbols meaning non-exact differentials, meaning the function has a value that depends on the integration path), Q = heat, W = mechanical or other work (electrical, magnetic, elastic, etc.).

- Second principle: $\delta S = \dfrac{\bar{\delta}Q}{T}$, for reversible processes; ($\delta S \geq \dfrac{\bar{\delta}Q}{T}$ for irreversible ones)

  - Together they lead to the fundamental relation: $T\delta S = \delta U + p\delta V + \bar{\delta}W$ (1)

The additivity principle (= if the system doubles its size, or its extensive parameters double, the energy doubles also), implies that the energy U(N,V,S) is an homogeneous function of the first order:

$$U(\lambda N, \lambda V, \lambda S) = \lambda U(N,V,S)$$

This leads to the Euler equation, obtained by differentiating this expression with respect to λ, then making λ = 1, integrating and using the third principle S(T=0) = 0:

$$U = \mu N - pV + TS \quad \text{(Euler eq.)}$$

The intensive parameters are the partial derivatives of U:

Chemical potential: $\mu = \partial U/\partial N$

Pressure: $p = - \partial U/\partial V$

Temperature $T = \partial U/\partial S$

which are the conjugate variables of N, V and S, the normal variables of the energy, as a thermodynamic potential.

The differential of Euler eq. together with the fundamental eq. (1), leads to the Gibbs-Duheim equation: $SdT - Vdp + Nd\mu = 0$ (2)

b) *Thermodynamic potentials*

   The thermodynamic potentials are important functions of the extensive (S, V, N) and intensive (μ, p, T) that describe the state of the system. Thermodynamic equilibrium, i.e., when the system stops evolving after a perturbation, corresponds to a minimum of the potential. For example for the energy U(x): $\partial U/\partial x = 0$ and $\partial^2 U/\partial x^2 > 0$

   In differential and integral form (repeated indices meaning summation over all types of particles) the commonly used potentials are:

Energy U(S,V,N$_j$): $dU = TdS - pdV + \mu_j dN_j$; $U = TS - pV + \mu_j N_j$

Helmholtz free energy F(T,V, N$_j$): $dF = -SdT - pdV + \mu_j dN_j$; $F = U - TS = \mu_j N_j - pV$

Gibbs free energy G(T, p, N$_j$): $dG = - SdT + Vdp + \mu_j dN_j$; $G = U - TS + pV = \mu_j N_j$

Omega potential Ω(T, V, μ_j): $d\Omega = -SdT - pdV - N_j d\mu_j$; $\Omega = F - G = -pV$

   When should we use one potential or another? Any potential can be used to define equilibrium. However it is best to use the potential whose natural variables remain constant. For example, Ω(T, V, μ_j) is to be used in open systems (with V and T constant), where N$_j$ varies but where μ_j stays constant.

Surface tension

Surface tension, denoted by γ, is defined as the energy to create a unit of surface.
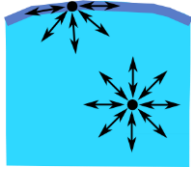
The energy of a surface arises from the broken bonds of the surface atoms, and /or from the missing attraction forces from the atoms or molecules outside the solid. To break a piece of matter and create a surface cost the energy of the bonds being broken. The surface tension has units of energy/area or force/length. It can be viewed as a force acting per unit length on any line dividing the surface.
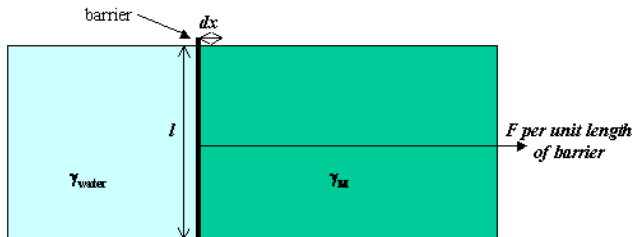
Droplets and bubbles:
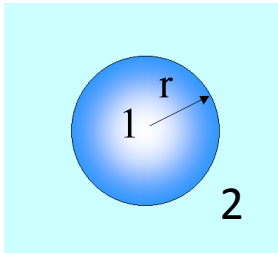
Lets consider two phases 1 and 2, separated by a surface of area A, in equilibrium. Since μ and T are constant we use the Omega potential (we could use also the Helmholtz potential F):
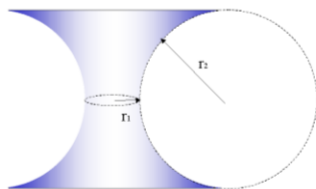
$$\Omega = -p_1 V_1 - p_2 V_2 + \gamma A$$

Since $V_1 + V_2 = $ constant, $d\Omega = -(p_1 - p_2)dV_1 + \gamma dA = 0$, in equilibrium.
For a planar surface this means $p_1 = p_2$, since $dA = 0$. For a spherical droplet or bubble, $V_1 = 4/3\pi r^3$, and $A = 4\pi r^2$, we obtain: $\mathbf{p_1 - p_2 = 2\gamma/r}$ (3)

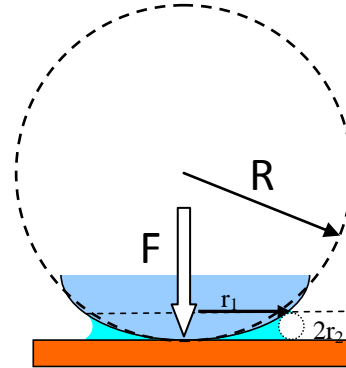For bubbles $r < 0$, and for a liquid filament (like that on the figure on the left),

$r_1 > 0$, and $r_2 < 0$, therefore

$$\mathbf{p_1 - p_2 = \gamma/r_1 - \gamma/r_2}\qquad (4)$$

For a soap bubble of similar shape and with open top and bottom ends $p_1 = p_2 = 1$ atmosphere, so that $r_1 = r_2$

Exercise 1: Calculate the pressure due to capillary condensation at the apex of a sphere (or for example an AFM tip):

Answer: *?*

Exercise 2: Find the geometrical relation between γ, force acting per unit length, and the increase in pressure in the concave side of a curved interface.
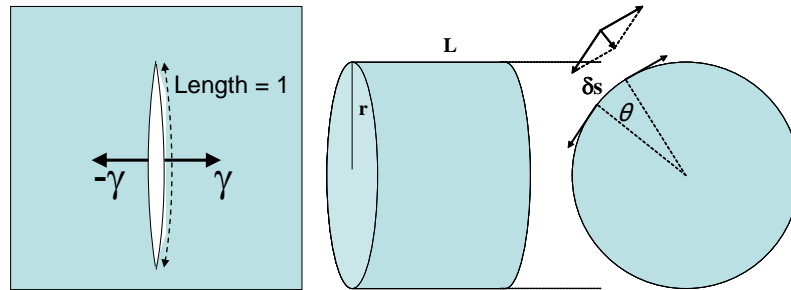
Answer:

We can explain Δp as the result of the pull from γ (= force per unit length, left figure) perpendicular to any line segment on the surface. For a "cut" perpendicular to a **principal radius of curvature** r, this produces a force towards the center f ~ γ.L.θ = γ. L.δs/r. The increase in pressure is f/(δs.L) = γ/r. The same reasoning for the pull on a line segment along the other principal curvature of radius r' will add another term γ/r'.

Equilibrium gas pressure

The pressures p_1 and p_2 near a curved surface are therefore different from the pressure of the gas over a flat surface, which defines the equilibrium vapor pressure p_0. Let's calculate the difference between p_1 and p_2 and p_0.

We start with the equilibrium condition of equal chemical potentials:

For the drop and the surrounding gas phase: $\mu_1(p_1,T) = \mu_2(p_2,T)$, (5)

For a flat surface and the gas phase: $\mu_1(p_0,T) = \mu_2(p_0,T)$, (6)

Combining we get: $\mu_1(p_1,T) - \mu_1(p_0,T) = \mu_2(p_2,T) - \mu_2(p_0,T)$

For small differences in pressure, by series expansion, and using the equality: $v = -\partial\mu/\partial p$, ($v$ = volume per molecule) we get:

$$v_1\delta p_1 = v_2\delta p_2,$$

where $\delta p_j \equiv p_j - p_0$. Since from (3) we know that $\delta p_1 - \delta p_2 = 2\gamma/r$, substituting gives:

$$\delta p_1 = \frac{2\gamma}{r} \cdot \frac{v_2}{v_2 - v_1} \approx \frac{2\gamma}{r},$$

Since the volume per gas phase molecule is around 3 orders of magnitude larger (at 1 atm) than that of a liquid phase molecule, i.e. $v_2 \gg v_1$,:

$$\delta p_2 = \frac{2\gamma}{r} \cdot \frac{v_1}{v_2 - v_1} \approx \frac{2\gamma}{r} \cdot \frac{v_1}{v_2}$$

Using the perfect gas equation: $pV = NkT$, we have $v_2 = kT/p_2 \sim kT/p_0$, so:

$$\delta p_{vap} = \frac{2\gamma v_{liq} p_0}{rkT}$$

This expression gives the increase in vapor pressure over a spherical droplet relative to that near a flat surface. Therefore, if there is a collection of droplets there can be no equilibrium. The big drops will grow at the expense of the small ones, since these would require higher vapor pressure around them. This is called **Ostwald ripening**.
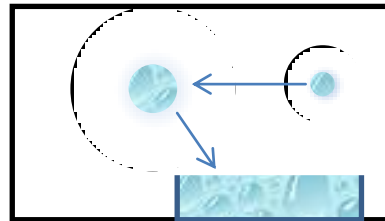
For very small droplets, we cannot use the approximation $v_1\delta p_1 = v_2\delta p_2$, since δp_2 can become quite large. We then need to use the unexpanded form of $\mu(p,T) = \mu(p_o,T) + kT\log(p/p_0)$ for the gas phase. With this we get the Kelvin equation:

$$\log \frac{p_{vapor}}{p_0} = \frac{2\gamma v_{liq}}{rkT}$$

Exercise 3: Find p_{vapor} for water ($\gamma = 73$ mJ/m^2) for droplets of radius 1000, 100, 10 Å.
Answer: For 100 Å the increase is 10%, and if r = 10 Å, it increases by a factor 2.7! That is why condensation will not occur even if equilibrium dictates it should (supercooling). This is the problem of nucleation.

Nucleation

Let's consider now the energy cost of nucleating a drop (or bubble) out of equilibrium, ($\mu_1 \neq \mu_2$). Upon condensation the free energy will increase by the amount:

$$\Delta F = \gamma A + (\mu_1 - \mu_2)N = 4\pi r^2\gamma + (\mu_1 - \mu_2)4/3\pi r^3/v_{liq}$$

Where N is the number of molecules condensed from the gas to the liquid.
If $\mu_1 > \mu_2$, no condensation can occur because ΔF increases always. However, if the vapor is supersaturated, then $\mu_1 < \mu_2$, and the cubic term is negative and ΔF goes through a maximum, corresponding to a droplet of a certain radius r_c. This can be found by differentiating giving:

$$r_c = 2\gamma v_{liq}/(\mu_2 - \mu_1),$$

which is, as expected, the value given by the Kelvin equation. The barrier for nucleation is: $\Delta F_{max} = 4/3.\pi r^2\gamma$
A density fluctuation can generate a nucleus of radius larger than r_c to nucleate a drop.

Lets calculate $\mu_1 - \mu_2$ over a droplet in a supersaturated vapor pressure $p_2 > p_o$ (p_o = saturation vapor pressure). We use: $\mu_2(p_2,T) = \mu_2(p_o,T) + kT\ln(p_2/p_o)$, and we assume that $\mu_1(p_1,T)$ for the droplet phase is equal to that of the flat bulk liquid $\mu_1(p_o,T)$, the difference being negligible. Since over the flat bulk (far away from the droplet-vapor area) $\mu_1(p_0,T) = \mu_2(p_0,T)$, we have:

$$\mu_2(p_2,T) - \mu_1(p_1,T) = kT\ln(p_2/p_o)$$

So that:

$$\Delta F = \gamma A + (\mu_1 - \mu_2)N = 4\pi r^2\gamma + (\mu_1 - \mu_2)4/3\pi r^3/v_{liq} = 4\pi r^2\gamma - kT\ln(p_2/p_o)4/3\pi r^3/v_{liq}$$
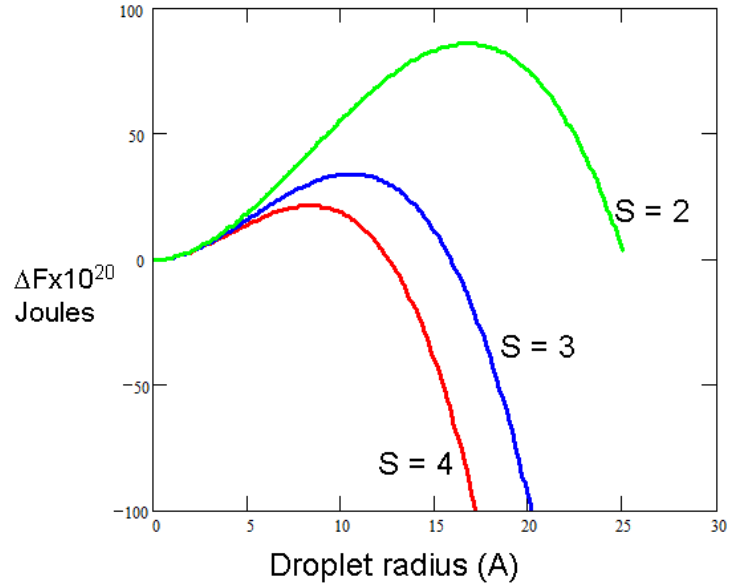
The graph above shows ΔF as a function of drop radius for various values of the supersaturation vapor pressure $S = p_2/p_o$ for water. As we can see, the maximum decreases and shifts to lower radius with S.